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# Reactions of alkyl-iron(II) and -ruthenium(II) complexes with $B(C_6F_5)_3$ and its water adducts. X-ray structure of a cyclometallated-iron(II) carbene

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## Abstract

The reactions of  $cis, trans - [M(CO)_2(PMe_3)_2CH_3I]$  [M = Fe (1), Ru (2)] and  $cis, trans, cis - [Fe(CO)_2(PMe_3)_2(CH_3)_2]$  (3) with  $B(C_6F_5)_3$  involve Me-abstraction from the metal with formation of reactive species that undergo decomposition processes. In the presence of H<sub>2</sub>O complex 2 reacts with  $B(C_6F_5)_3$  forming  $cis, trans - [Ru(CO)_2(PMe_3)_2I(HOB(C_6F_5)_3)]$  (7) that slowly transforms in  $cis, trans - [Ru(CO)_2(PMe_3)_2I(HOB(C_6F_5)_3)]$  (7) that slowly transforms in  $cis, trans - [Ru(CO)_2(PMe_3)_2I(HOB(C_6F_5)_3)]^-$  (8), while complex 1 affords the cyclometallate complex  $trans - [Fe(CO)(PMe_3)_2I(=C(Me)-O-B(C_6F_5)_2-OH-)]$  (9) whose molecular structure was investigated by X-ray diffraction studies. © 2003 Elsevier B.V. All rights reserved.

Keywords: Cyclometallated-iron(II) carbene; B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> activation; B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>·H<sub>2</sub>O reactivity

## 1. Introduction

There is great interest in the synthesis of electrophilic transition metal complexes due to their strong catalytic activity in the polymerization of olefins [1] and in the activation of C–H and C–C bonds [2]. Pentafluorophenyl boranes are important systems for increasing the electrophilicity of transition metal alkyl complexes [3,4] and they are commonly used as co-catalysts in metallocene-based processes for the homogeneous polymerization of olefins [5]. Many studies have been carried out on the structure of the species responsible for the catalytic activity [6] of the metallocene alkyl complexes of the early transition metals. Fewer studies have been carried out on the activation of the late transition metals with pentafluorophenylboranes; the activation of molybdenum [7a], chromium [7b], nickel [7c] and platinum

[7d] was only recently described. In all the cases, the activation of the alkyl complexes leads to the formation of contact ion pairs in which the Lewis acid is bonded to an alkyl group [6,8]. The presence of  $H_2O$  affects the reactivity of pentafluoroboranes [9] and this has been attributed to the formation of water adducts, which act as strong acids [10].

In this work we present the results of our studies on the reactivity of  $B(C_6F_5)_3$  and its water adducts with the isostructural and isoelectronic iron and ruthenium complexes *cis*,*trans*-[M(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(Me)I] [M = Fe (1), Ru (2)] and *cis*,*trans*,*cis*-[Fe(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(Me)<sub>2</sub>] (3).

# 2. Experimental

Complexes cis, trans-[Fe(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>I] (1) [11,12], cis, trans-[Ru(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>I] (2) [13] and cis, trans, cis-[Fe(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] (3) [14] were prepared as described in the literature. Hydrated adducts of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> were obtained by adding H<sub>2</sub>O in n-hexane.

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Benzene and n-hexane were dried by distillation over sodium chips [15].  $CH_2Cl_2$ , 1-pentene and cyclopentene were dried by distillation over  $P_2O_5$  [15]. The course of the reactions was followed by IR and NMR spectroscopies by using a 1725 × Perkin Elmer spectrophotometer and a Bruker DRX 400 spectrometer, respectively.

One- and two-dimensional <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C and <sup>19</sup>F NMR spectra were measured on a Bruker DPX 200 or Bruker DRX 400 spectrometer; referencing is relative to TMS (<sup>1</sup>H and <sup>13</sup>C), CCl<sub>3</sub>F (<sup>19</sup>F) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). NMR samples were prepared by dissolving about 20 mg of the compounds in 0.5 ml of deuterated solvent. Twodimensional <sup>1</sup>H NOESY and <sup>19</sup>F, <sup>1</sup>H HOESY spectra were recorded with a mixing time of 500–800 ms. Elemental analyses were carried out using a Carlo Erba 1106 elemental microanalyzer.

# 2.1. Reaction of cis, trans-[ $Fe(CO)_2(PMe_3)_2CH_3I$ ] (1) and $B(C_6F_5)_3$

100 mg of complex 1 were added to an equimolar solution of  $B(C_6F_5)_3$  in  $C_6D_6$  at room temperature (r.t.). Immediate precipitation of a yellow solid was observed. The <sup>1</sup>H NMR spectrum of the solution shows a triplet at 1.69 ppm ( $|^2J_{HP}+^4J_{HP}|=7.5$  Hz) and a broad band at 0.73 ppm; in IR two CO stretching frequencies are observed at 2014 and 1964 cm<sup>-1</sup>. After a few minutes the precipitation was complete. The solution was decanted and the solid was dried and dissolved in CD<sub>2</sub>Cl<sub>2</sub>. In this solution complexes **4** and **5** are recognized by their IR and NMR spectra, previously described [11,16].

## 2.1.1. Complex 4

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  1.72 (t Harris, <sup>11</sup>|<sup>2</sup>J<sub>HP</sub>+<sup>4</sup>J<sub>HP</sub>| = 8.8, PMe<sub>3</sub>), 0.54 (broad band, MeB), 0.14 (t, <sup>3</sup>J<sub>HP</sub> = 7.8, CH<sub>3</sub>); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  -133.30 (s, *o* F), -165.35 (s, *p* F), -167.74 (s, *m*F); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  15.12 (s, PMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  208.44 (t, <sup>2</sup>J<sub>CP</sub> = 24.8, CO), 203.6 (t, <sup>2</sup>J<sub>CP</sub> = 14.1, CO); IR (CD<sub>2</sub>Cl<sub>2</sub>):  $\nu_{CO} = 2085$ , 2021 cm<sup>-1</sup>.

# 2.1.2. Complex 5

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  1.60 (t Harris,  $|{}^{2}J_{HP} + {}^{4}J_{H-P}| = 7.9$ , *trans* PMe<sub>3</sub>), 1.51 (d,  ${}^{2}J_{HP} = 8.4$ , PMe<sub>3</sub>), 0.54 (broad, BMe), -0.14 (dt,  ${}^{3}J_{HP} = 8.1$ ,  ${}^{3}J_{HP} = 10.5$ , CH<sub>3</sub>); <sup>19</sup>F NMR(CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  -133.30 (s, *o* F), -165.35 (s, *p* F), -167.74 (s, *m* F); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  15.91 (d,  ${}^{2}J_{PP} = 65.8$ , PMe<sub>3</sub>), 11.40 (t,  ${}^{2}J_{PP} = 62$ , PMe<sub>3</sub>); IR(CD<sub>2</sub>Cl<sub>2</sub>):  $v_{CO} = 2018$ , 1965 cm<sup>-1</sup>.

# 2.2. Reaction of cis, trans, cis-[ $Fe(CO)_2(PMe_3)_2(CH_3)_2$ ] (3) and $B(C_6F_5)_3$

100 mg of complex **3** were added at r.t. to a  $C_6D_6$  solution containing equimolar amount of  $B(C_6F_5)_3$ . Precipitation of a brown oil was immediately observed. The <sup>1</sup>H NMR spectrum of the solution showed broad resonance at 1.34 ppm, assigned to PMe<sub>3</sub>, and at 0.56 ppm, assigned to the Fe–Me–B group, with an intensity ratio of 3/1. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at 39.58 ppm. The solution was decanted and the brown oil was dissolved in CD<sub>2</sub>Cl<sub>2</sub>. The formation of complexes **4** and **5** was observed.

# 2.3. Reaction of cis, trans- $[Ru(CO)_2(PMe_3)_2CH_3I]$ (2) and $B(C_6F_5)_3$

100 mg of complex **2** were added to a  $C_6D_6$  solution of equimolar amount of  $B(C_6F_5)_3$ . Immediate formation of a brown oil was observed. The <sup>1</sup>H NMR spectrum of the solution shows a Harris triplet at 1.59 ppm  $(|^2J_{HP} + ^4J_{HP}| = 6.7 \text{ Hz})$  and a broad band at 0.40 ppm. The brown oil was dissolved in  $CD_2Cl_2$ . The final product was complex **6**, which was characterized by NMR [17].

# 2.3.1. Complex 6

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  1.74 (t Harris,  $|{}^{2}J_{HP} + {}^{4}J_{HP}| = 7.9$ , PMe<sub>3</sub>), 0.53 (broad, BMe), -0.10 (t,  ${}^{3}J_{HP} = 7.1$ , RuCH<sub>3</sub>); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  -133.47 (s, *o* F), -165.62 (s, *p* F), -168.1 (s, *m*F); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  -11.55 (s, PMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  194.2 (t, <sup>2</sup>*J*<sub>CP</sub> = 19.6, 2CO), 187.84 (t, <sup>2</sup>*J*<sub>CP</sub> = 8.1, CO); IR (CD<sub>2</sub>Cl<sub>2</sub>): *v*<sub>CO</sub> = 2115, 2045 cm<sup>-1</sup>.

In another experiment, the reaction was carried out in n-pentene as a solvent in order to stabilize the intermediate. No difference was observed with respect to the reaction carried in  $C_6D_6$ : both the intermediate and final product were the same.

#### 2.4. Preparation of complexes 7 and 8

170 mg of complex **2** were dissolved in n-hexane. An equimolar amount of  $H_2O \cdot B(C_6F_5)_3$  in n-hexane solution was added at r.t. to the stirred solution of the ruthenium complex. An instantaneous reaction was observed with the formation of a yellow precipitate. The solution was left at r.t. for 1 h to allow complete precipitation of the solid. The solid (complex 7) was separated by filtration (150 mg of yellow crystals, yield: 32%). Anal. Found: C, 32.79; H, 2.05. Calc. for  $C_{26}H_{20}BF_{15}IO_3P_2Ru: C, <math>32.3$ ; H, 2.09%.

# 2.4.1. Complex 7

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, *J* values in Hz):  $\delta$  2.74 (septet, <sup>5</sup>*J*<sub>HF</sub> = 3.4, OH), 1.14 (t Harris,  $|^{2}J_{HP} + {}^{4}J_{HP}| =$  7.9, PMe<sub>3</sub>); <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, *J* values in Hz):  $\delta$  -131.46 (s,  $\sigma$ F), -158.24 (t,  ${}^{3}J_{FF} = 20.7, p$ F), -163.78 (dd,  ${}^{3}J_{FF} = 18.8, {}^{3}J_{FF} = 20.7, m$ F);  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, *J* values in Hz):  $\delta$  (ppm), -13.79 (s, PMe<sub>3</sub>); <sup>13</sup>C{}^{1}H{} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, *J* values in Hz):  $\delta$  196.5 (t,  ${}^{2}J_{CP} = 13.6$ , CO), 188.41 (t,  ${}^{2}J_{CP} = 10.9,$  CO), 148.23 (d,  ${}^{1}J_{CF} = 226.0, \sigma$ C), 140.35 (d,  ${}^{1}J_{CF} = 248.9, p$ C), 137.88 (d,  ${}^{1}J_{CF} = 349.0, m$ C), 121.7 (s, *Cipso*), 16.32 (t Harris,  $|{}^{1}J_{CP} + {}^{3}J_{CP}| = 33.6, PMe_3$ ).

Complex 7 was rather stable in benzene; in hydrated  $CH_2Cl_2$  it reacted slowly with  $H_2O$  to form complex 8, which was characterized by NMR.

#### 2.4.2. Complex 8

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  5.14 (s, H<sub>2</sub>O), 5.7 (s, OH+2H<sub>2</sub>O), 1.82 (t Harris, |<sup>2</sup>J<sub>HP</sub>+<sup>4</sup>J<sub>HP</sub>| = 7.9, PMe<sub>3</sub>); <sup>19</sup>F NMR(CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  -133.50 (d, <sup>3</sup>J<sub>FF</sub> = 18.8, *o*F), -165.70 (t, <sup>3</sup>J<sub>FF</sub> = 20.3, *p*F), -168.2 (dd, <sup>3</sup>J<sub>FF</sub> = 18.6, <sup>3</sup>J<sub>FF</sub> = 20.3, *m*F); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz):  $\delta$  195.6 (t, <sup>2</sup>J<sub>CP</sub> = 12.3, CO), 189.4 (t, <sup>2</sup>J<sub>CP</sub> = 10.6, CO), 148.2 (d, <sup>1</sup>J<sub>CF</sub> = 225.0, *o*C), 139.7 (d, <sup>1</sup>J<sub>CF</sub> = 247.0, *p*C), 137.17 (d, <sup>1</sup>J<sub>CF</sub> = 254.0, *m*C), 121.26 (s, *Cipso*), 16.53 (t Harris, |<sup>1</sup>J<sub>CP</sub>+<sup>3</sup>J<sub>CP</sub>| = 34.4, PMe<sub>3</sub>).

## 2.5. Preparation of complex 9

200 mg of complex 1 were dissolved in n-hexane at r.t. A solution containing  $B(C_6F_5)_3$  and  $H_2O$  (molar ratio = 0.5) was added. A precipitate formed immediately. The solution was left at -18 °C for 12 h to complete the precipitation. The solid was separated and washed with cold n-hexane. The solid was extracted with cyclopentene. Orange crystals of complex 9 precipitated from the solution in cyclopentene at -18 °C (yield 20%). The molecular structure of complex 9 in the solid state was determined by X-ray diffractometric methods (see infra). Anal. Found: C, 33.01; H, 3.00; Calc. as  $C_{21}H_{22}BF_{10}IO_3P_2Fe: C, 32.85; H, 2.89\%$ .

# 2.5.1. Complex 9

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz): δ 3.03 (t, <sup>4</sup>*J*<sub>HP</sub> = 0.8, CH<sub>3</sub>), 1.46 (t Harris,  $|{}^{2}J_{HP} + {}^{4}J_{H-P}| = 8.2$ , PMe<sub>3</sub>), 1.30 (broad, OH); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz): δ -135.14 (d,  ${}^{3}J_{FF} = 14.8$ , *o*F), -157.49 (t,  ${}^{3}J_{FF} = 19.9$ , *p*F), -163.46 (dd,  ${}^{3}J_{FF} = 14.8$ ,  ${}^{3}J_{FF} = 19.9$ , *m*F);  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz): δ 5.84 (s, PMe<sub>3</sub>);  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K, *J* values in Hz): δ 340.6 (t,  ${}^{2}J_{CP} = 21.2$ , Fe=C), 219.3 (t,  ${}^{2}J_{CP} = 33.2$ , CO), 147.2 (d,  ${}^{1}J_{CF} = 241.3$ , *o*C), 140.4 (d,  ${}^{1}J_{CF} = 290.6$ , *p*C), 137.7 (d,  ${}^{1}J_{CF} = 215.5$ , *m*C), 101.28 (t,  ${}^{2}J_{CF} = 22.1$ , *Cipso*), 44.4 (s, Me), 17.01 (t Harris,  $|{}^{1}J_{CP} + {}^{3}J_{CP}| = 28.9$ , PMe<sub>3</sub>). IR (n-hexane):  $v_{CO} = 1950$  cm<sup>-1</sup>.

## 2.6. X-ray crystallography

Crystals of 9 suitable for X-ray single crystal studies were precipitated from cyclopentene at -18 °C. Crystal data and details of structure refinement are reported in Table 1. Diffraction intensities were collected at 293 K on a Bruker AXS SMART 2000 CCD diffractometer using graphite monochromated Mo Ka radiation. The data were collected using  $0.3^{\circ}$  wide  $\omega$  scans, crystal-todetector distance of 5.0 cm, and corrected for absorption empirically using the SADABS routine. Data collections nominally covered a full sphere of reciprocal space with 10 s exposure time per frame. The structure was solved by direct methods and refined on  $F^2$  by fullmatrix least-squares calculations using the SHELXTL/PC package [18]. Thermal vibrations were treated anisotropically. Unambiguous location of the hydrogen atom bound to O(2) has been made possible from both the quality of the crystal data and redundancy of reflections collected. The remaining H atoms were geometrically positioned [C-H 0.96 Å] and refined "riding" on their corresponding carbon atoms. Refinement converged at a final R = 0.033,  $wR^2 = 0.069$ , S = 1.01. Molecular graphics were prepared using ORTEP3 for WINDOWSNT [19].

Table 1					
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Crystal data and details of refinement for complex 9

Empirical formula	$C_{21}H_{22}BF_{10}FeIO_3P_2$
Fw	767.89
Temperature (K)	293
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.796(2)
b (Å)	17.631(3)
c (Å)	18.335(3)
β(°)	97.68(2)
Volume ( $Å^3$ )	2817.6
Z	4
Density (Mg $m^{-3}$ )	1.810
<i>F</i> (000)	1504
Crystal size (mm)	$0.2 \times 0.3 \times 0.3$
$\theta$ Range for data collection (°)	2-34
Index range	$-13 \le h \le 13, -21 \le k \le 27, -$
-	$28 \le l \le 28$
Number of reflections collected	39 551
Number of data/restraints/para-	10 605/0/333
meters	
Goodness-of-fit on $F^2$	1.013
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R = 0.0332, wR^2 = 0.0695$
Largest difference peak and hole	0.53-0.50
$(e Å^{-3})$	

## 3. Results and discussion

By the reactions of complex 1, 2 or 3 with  $B(C_6F_5)_3$  in  $C_6D_6$  at room temperature a brown solid or liquid immediately precipitated. The <sup>1</sup>H NMR spectra of the supernatant  $C_6D_6$  solutions indicated the formation of B-Me bond by attack of  $B(C_6F_5)_3$  to the methyl ligand as supported by the presence of a broad resonance at approximately 0.5–0.6 ppm typical of  $MeB(C_6F_5)_3^$ anion [20]. Attempts to trap the intermediates [21] carrying out the reactions in n-pentene were unsuccessful; other more nucleophilic ligands, such as carbon monoxide and phosphine could not be used to stabilize the intermediates because they react quickly with the starting methyl-complexes affording acetyl complexes [22].

The precipitates from  $C_6D_6$  solutions dissolved in  $CD_2Cl_2$  showed the presence of complexes 4 and 5 in a 3/1 ratio in the case of reagents 1 and 3 and complex 6 in the case of reagent 2 (Chart 1) as indicated by IR and <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopies and by the comparison with the previously described [11,16,17] complexes containing BPh<sub>4</sub><sup>-</sup> as counteranion. The formation of complexes 4, 5, and 6 in low yield can only be explained by assuming that the intermediates coming from B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> attack on metal–Me group undergo decomposition processes with a redistribution of PMe<sub>3</sub> and CO ligands.

With the suspicion that the decomposition processes could be due to the presence of adventitious water, we decided to carry out the reactions of complexes 1, 2, and 3 with H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, prepared as reported in the literature [23]. The <sup>1</sup>H NMR spectrum of the water adduct in CD<sub>2</sub>Cl<sub>2</sub> shows a resonance at 6.7 ppm, assigned to H<sub>2</sub>O coordinated to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; the <sup>19</sup>F NMR spectrum shows resonances at -133.8 ppm (*o*F), -152.6 ppm (*p*F) and -163.0 ppm (*m*F), which are very near to those assigned to this compounds in the literature [10,23]. The <sup>19</sup>F, <sup>1</sup>H HOESY spectrum shows a strong contact between the *ortho* fluorine atoms and the water protons, confirming the structure.

While the reactions of iron(II) alkyl complexes did not afford clear results, the reaction of H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with complex **2** in n-hexane gave a yellow precipitate which was tentatively characterized as **7** (Chart 1), in which a coordination position of ruthenium is occupied by the oxygen of the [HOB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> anion. Structure **7** was deduced on the basis of an elemental analysis and of IR and NMR spectra in C<sub>6</sub>D<sub>6</sub>. The <sup>1</sup>H NMR spectrum shows a septet at 2.74 ppm assigned to the OH proton, which couples with 6 equiv. *ortho* fluorines of C<sub>6</sub>F<sub>5</sub> [24] (<sup>5</sup>J<sub>H-F</sub> = 3.4 Hz) and a deceptive triplet at 1.14 ppm due to two phosphine ligands [25]. The IR spectrum shows two CO stretching bands of equal intensity at 2051 and 1991 cm<sup>-1</sup>, indicating two *cis* CO ligands. This is confirmed by the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum which shows







Fig. 1.  ${}^{19}$ F,  ${}^{1}$ H HOESY NMR spectrum (302 K, methylene chlorided<sub>2</sub>) of the mixture of complexes **7** and **8**.

two triplets at 196.5 and 188.41 ppm coupled to 2 equiv. *trans* phosphine ligands. The <sup>19</sup>F,<sup>1</sup>H HOESY spectrum in  $CD_2Cl_2$  shows strong contacts between the *ortho* fluorine atoms and the OH and PMe<sub>3</sub> protons, indicating an intramolecular structure for these interacting groups. The presence of the Ru–I bond was verified by the precipitation of AgI after the decomposition of complex 7 with HNO<sub>3</sub> in H<sub>2</sub>O and the addition of AgNO<sub>3</sub>.

The formation of complex 7 by reaction with  $H_2O$ · $B(C_6F_5)_3$  is attributed to the strong Bronsted acid character of the coordinated  $H_2O$  [26] which is able to protonate the methyl group bonded to the metal center as previously observed by Puddephatt et al. in square planar dimethyl platinum complexes [27].

Complex 7 is rather stable in benzene, but in wet  $CH_2Cl_2$  it reacts slowly with  $H_2O$  to give complex 8, in which the OH bond to ruthenium is replaced by H<sub>2</sub>O (Chart 1). The <sup>1</sup>H NMR spectrum of **8** in  $CD_2Cl_2$  shows a band at 5.14 ppm (integrating for two protons) assigned to coordinated H<sub>2</sub>O, a band at 5.7 ppm (integrating for five protons) assigned to the OH of the anion  $[HOB(C_6F_5)_3]^-$ , bonded by hydrogen bond to two  $H_2O$  (see Fig. 1) and a deceptive triplet (integrating for 18 protons) assigned to two trans PMe<sub>3</sub> ligands. The <sup>19</sup>F,<sup>1</sup>H HOESY spectrum shows strong contacts between the ortho and meta fluorine atoms and the OH proton and very weak contacts between the ortho and meta fluorine atoms and the PMe<sub>3</sub> protons; this behavior is explained by the formation of contact ion pairs [28]. A comparison of the intensity of the contacts in complexes 7 and 8 clearly shows that in complex 7 all the contacts are intramolecular, while in complex 8 the OH gives intramolecular contacts and PMe<sub>3</sub> gives intermolecular contacts with the fluorine atoms (Fig.



Fig. 2. ORTEP diagram of complex 9.

Table 2 Selected bond distances (Å) and angles (°) for complex  ${\bf 9}$ 

Bond distances	
Fe-I	2.6720(4)
Fe-C(7)	1.718(3)
Fe-C(8)	1.840(2)
Fe-O(2)	2.012(2)
Fe-P(2)	2.276(1)
Fe-P(1)	2.280(1)
B-O(2)	1.472(3)
B-O(3)	1.498(3)
B-C(10)	1.659(3)
B-C(16)	1.663(3)
Bond angles	
C(7) - Fe - C(8)	95.4(1)
C(7)-Fe-O(2)	175.9(1)
C(8)-Fe-O(2)	80.5(1)
C(7)-Fe-P(2)	88.9(1)
C(8)-Fe-P(2)	93.7(1)
O(2)-Fe-P(2)	91.2(1)
C(7)-Fe-P(1)	88.9(1)
C(8)-Fe-P(1)	92.3(1)
O(2)-Fe-P(1)	91.3(1)
P(2)-Fe-P(1)	173.84(3)
C(7)-Fe-I	93.3(1)
C(8)-Fe-I	171.2(1)
O(2)-Fe-I	90.72(5)
P(2)-Fe-I	86.81(2)
P(1)-Fe-I	87.52(2)
O(2)-B-O(3)	102.4(2)
O(2) - B - C(10)	113.3(2)
O(3)-B-C(10)	109.5(2)
O(2)-B-C(16)	113.9(2)
O(3)-B-C(16)	109.1(2)
C(10)-B-C(16)	108.4(2)

1). The contact between the *ortho* fluorine and  $H_2O$  coordinated to the metal is very intense because it is exchanging with the  $H_2O$  bonded to OH by hydrogen bond (Fig. 1).

When the H<sub>2</sub>O content is less than equimolar with respect to H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, the course of the reaction is different. The clearest results are obtained with complex **1**. Complex **1** reacts instantaneously in n-hexane with the formation of *trans*-[Fe(CO)(PMe<sub>3</sub>)<sub>2</sub>I(=C(Me)-O-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-OH-)] (9) (Chart 1) which in IR shows a carbonyl stretching at 1950 cm<sup>-1</sup>.

The molecular structure of 9, obtained by a single crystal X-ray diffraction study, is given in Fig. 2, together with its crystallographic numbering. Table 2 reports selected bond distances and angles. The iron atom is in the oxidation state +2 and the negative charges are formally localized on the iodide ligand and tetracoordinate boron. The iron atom exhibits the expected octahedral geometry with the trimethylphosphine ligands occupying trans positions. The equatorial sites contain the carbene and oxygen donors included in a five-membered -C(Me)-O-B-O(H) chelate ring. The iodide and carbonyl ligands occupy the sites trans to the carbene and oxygen, respectively. The idealized molecular symmetry is  $C_s$  and also the groups appended to the coordinated atoms conform to this symmetry. The five-membered chelate ring represents one of the few examples of cyclometallate iron carbenes and the only one containing the  $B(C_6F_5)_2$  fragment [29]. The ring is strictly planar [rms deviation of all five atoms 0.01 Å] with the O(2)-Fe-C(8) and O(2)-B-O(3) angles of 80.5(1) and 102.4(2)°, respectively. The Fe-C(carbene) bond [1.840(2) Å] is comparable with the numerous values reported for other Fe-C(O)R interactions in Fe(II) complexes [average 1.895 Å] [29]. The double bond character of this interaction is well appreciated from a comparison of the Fe-C(carbonyl) bond in our complex [1.718(3) Å] and the Fe–C(methyl) bond in Fe(II) complexes [29] [average value 2.083 Å, cfr. 2.093 and 2.083 Å in cis, trans- and trans, trans-[Fe(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)I] [30]. A stereochemically and electronically comparable situation has been found in Fe(CO)(PEt<sub>3</sub>)<sub>2</sub>(Cl)[C(OSiMe<sub>3</sub>)CHCOOMe] [31]. An analysis of the iron-ligands distances shows strictly equivalent values for the Fe-P [2.276(1) and 2.280(1) Å against 2.276(1) and 2.272(1) Å] and Fe-C(carbonyl) interactions [1.718(3) vs. 1.728(4) Å] and slightly shorter Fe-C(carbene) and Fe-O values in our compound [1.840(2) and 2.012(2) Å against 1.899(4) and 2.040(3) Å]. Very probably the more localized nature of the  $\pi$ bonds in the ring including a tetracoordinate boron increases the Fe-C(carbene) and Fe-O bond orders with respect to what found in the completely delocalized system in Fe(CO)(PEt<sub>3</sub>)<sub>2</sub>(Cl)[C(OSiMe<sub>3</sub>)CHCOOMe] [31]. A very similar carbene grouping has been recently reported in  $[Fe(C_5H_5)(CO)\{k^2(C, O)-C(OMe)C_6H_4-o-$  O-Me}][OTf] [32]. Here the Fe-C(carbene), 1.859(6), and Fe-O, 2.045(5) Å, distances are again slightly longer than in 9, while the C(carbene)-C(ring), 1.484(8), and C (carbene)-O(methoxy), 1.299(7) Å, values are strictly comparable with the C(carbene)-C(methyl) and C(carbene)-O(ring) [1.499(3) and 1.297(3) Å] distances in our complex.

Concerning the other bond distances in the fivemembered ring, the short O–C(carbene) distance [1.297(3) Å] shows neat multiple bond character, while the O–B interactions are non-equivalent single bonds [1.472(3) and 1.498(3) Å]. Short intramolecular Hbonding interactions occur between O(2)–H(2) and both F(1) and F(10) atoms [O···F distances 2.822 and 2.774, O–H···F angles 113.9 and 115.6°, respectively]. Also C–H···F interactions occur both of intra-molecular, C(1) with F(10) [C···F distance 3.32 Å, C–H···F angle 161.9°], and inter-molecular kind, C(2) with symmetry-related F(2) [C···F distance 3.45 Å, C– H···F angle 170.3°].

The solution structure of complex 9 was determined by NMR spectroscopy. The <sup>1</sup>H NMR spectrum shows a triplet at 3.03 ppm assigned to the Fe=C(Me)-group, which couples to 2 equiv. phosphorus atoms; the carbene structure is supported by the  ${}^{4}J_{H-P}$  coupling, which is not observed in the acetyl complexes [17]. A deceptive triplet, typical of 2 equiv. PMe<sub>3</sub> ligands, is observed at 1.46 ppm. The band at 1.30 ppm is assigned to the OH coordinated to iron, broadened by the coupling to quadrupolar boron. The <sup>19</sup>F,<sup>1</sup>H HOESY spectrum shows strong contacts between the ortho fluorine atoms and the OH and PMe<sub>3</sub> protons and weak contacts between the ortho fluorine atoms and the methyl carbene and between the meta fluorine atoms and the PMe<sub>3</sub> protons in agreement with the interatomic distances in complex 9. The most interesting aspect of the  ${}^{13}C{}^{1}H$  NMR spectrum is a triplet at 340.4 ppm, which is unusual and can be assigned to the carbene carbon [33].

The formation of complex 9 can be explained on the basis of Scheme 1. The first step of the reaction is the interaction of free  $B(C_6F_5)_3$  with the oxygen of the carbon monoxide (a), which catalyses the methyl migration [34] and stabilizes the carbone structure (b) [20]; H<sub>2</sub>O then binds to the free coordination site (c) and, finally, the elimination of  $C_6HF_5$  gives the cyclic structure 9 [35].

In conclusion, the first step of the reaction of complexes 1, 2 and 3 with  $B(C_6F_5)_3$  is the abstraction of methyl to form cation like complexes, which are very reactive and were not characterized. They continue to decompose forming the stable complexes 4, 5 and 6. In the presence of water, free H<sub>2</sub>O,  $B(C_6F_5)_3$ , H<sub>2</sub>O.  $B(C_6F_5)_3$  and other hydrated species are in equilibrium [10]. Under these conditions the behavior of complexes 1 and 2 is similar: all the reactions are possible with either



Scheme 1.

the formation of the ionic complexes 4, 5, 6 or the formation of complexes 7 and 9. The quantities of the complexes depend on the relative rates of the reactions and on the metal. In the case of complex 1, the formation of 9 is prevailing, while in the case of complex 2, the main product is complex 7.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 196048 for compound 9. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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